(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 492 987 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 91311805.5

(22) Date of filing: 19.12.91

(51) Int. Cl.[5]: C22C 9/00, H01L 23/495

(30) Priority: 20.12.90 JP 404416/90

(43) Date of publication of application: 01.07.92 Bulletin 92/27

(84) Designated Contracting States: DE FR GB

(71) Applicant: KABUSHIKI KAISHA TOSHIBA
72, Horikawa-cho Saiwai-ku
Kawasaki-shi Kanagawa-ken 210 (JP)

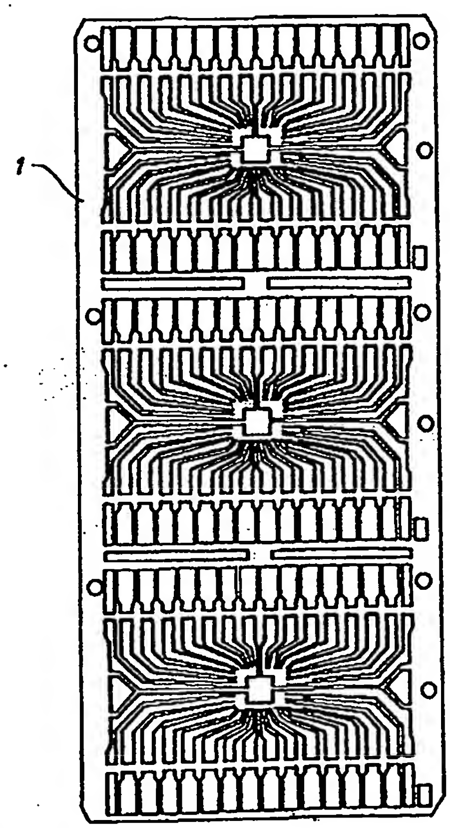
(72) Inventor: Nakashima, Nobuaki
Intellectual Property Div., Toshiba Corp.
1-1-1, Shibaura, Minato-ku, Tokyo (JP)
Inventor: Sugai, Shinzo
Intellectual Property Div., Toshiba Corp.
1-1-1, Shibaura, Minato-ku, Tokyo (JP)

(74) Representative: BATCHELLOR, KIRK & CO.
2 Pear Tree Court Farringdon Road
London EC1R 0DS (GB)

(54) **Copper alloys and lead frames made therefrom.**

(57) A copper alloy suitable for constructing lead frames containing 0.1 to 1 % by weight of chromium, 0.01 to 0.5% by weight of zirconium and having partial discoloured regions caused by unbalanced precipitation of the zirconium distributed thereon at a rate of 2 grains/100cm^2 or less. The lead frame is, for example, made by using an alloy containing 0.005% by weight of sulphur or less. The lead frame can have high reliability, high yield of production and high electrical conductivity, and is particularly suited for the production of integrated circuits.

FIG. 1



EP 0 492 987 A1

Jouve, 18, rue Saint-Denis, 75001 PARIS

The present invention relates to a lead frame and the material of which the frame is made, being a Cu alloy.

Recently, improvements in materials used for integrated circuits (IC) has made rapid progress, allowing highly integrated and mass-produced IC. In many fields, both material and components are required to be further improved because of the concern about properties and price.

For example, a lead frame made of a Fe-Ni alloy such as 42wt%Ni-Fe or 29wt%Ni-17wt%Co-Fe has a coefficient of thermal expansion very similar to that of the semiconductor element.

However, a lead frame made of a Fe alloy is expensive because expensive components such as nickel and cobalt are used. In addition, a lead frame made of a Fe alloy doesn't satisfy the requirements of high radiation, that is, thermal conductivity, which is required as semiconductors become highly integrated.

Accordingly, lead frames made of a Cu alloy are chiefly being used because of the property of high radiation and lower costs. In such lead frames made of a Cu alloy, Cu-Cr-Zr alloy is especially being used because of its high hardness and high conductivity.

However, the lead frame made of a Cu-Cr-Zr alloy as described above often has a peeling part on the surface of the lead frame, and a plating scab caused by heat treatment when the surface is coated. When an IC package or a LSI package with a lead frame of Cu-Cr-Zr alloy is made, because of the problems as described above, the yield of production and the reliability of these packages of a Cu-Cr-Zr alloy are impaired. Further more, a Cu-Cr-Zr alloy as described above is required to have high conductivity with a good producibility, for example not less than 75IACS%, for the high efficiency of a lead frame.

In view of this problem, the present inventors have made extensive studies, and found that the problems such as peeling parts on the surface of the lead frame and a scab on the lead frame caused by heat treatment when being plated and the like are due to the number of partial discoloured regions, and further more, the partial discoloured regions are due to the unbalanced precipitation of Zr.

The present invention has been made based on this finding and has for its object to provide a lead frame and a material of the same which has a high conductivity and which makes it possible to produce a highly reliable IC package or a LSI package and the like with a high yield of production.

A material of the present invention suitable for making a lead frame comprises a copper alloy which contains 0.1 to 1% by weight of Cr, 0.01 to 0.5% by weight of Zr and having a partial discoloured region caused by unbalanced precipitation of the Zr distributed thereon at a rate of 2 grains/100cm^2 or less. The invention also embraces a lead frame constructed of the aforesaid material.

In order that the invention may be illustrated and readily carried into effect, embodiments thereof will now be described by way of non-limiting example only with reference to the accompany drawings, wherein:

Fig. 1 is a plan view of a lead frame according to an embodiment of the present invention,

Fig. 2 is a typical view showing the microphotograph taken by scanning electron microscope of a surface of a lead frame according to a comparative example,

Fig. 3 is a microphotograph (x 32) of a surface of a comparative lead frame showing plating scabs caused by heat treatment,

Figs. 4a to 7b show results of element detection by EPMA on the same region of a surface of a comparative lead frame, whereby:-

- Fig. 4a show Zr detection,
- Fig. 4b shows Al detection,
- Fig. 5a shows S detection,
- Fig. 5b shows C detection,
- Fig. 6a shows P detection,
- Fig. 6b shows O detection,
- Fig. 7a shows Si detection, and
- Fig. 7b shows Cr detection.

The number of partial discoloured regions caused by unbalanced precipitation of Zr has been found to be an important feature in the present invention.

If the number of partial discoloured regions caused by unbalanced precipitation of Zr is 2 grains/100cm^2 or less, the problems such as plating scabs on the lead frame caused by heat treatment are improved, which makes it possible to produce a highly reliable IC package or LSI package and the like with a high yield of production. The number of these partial discoloured regions is preferably 1 grain/100cm^2 or less. The number of partial discoloured regions is more preferably zero. The phrase "partial discoloured regions caused by unbalanced precipitation of Zr" is used in this description and the claims to mean a region which has a different colour from other regions, which can be observed by microphotograph. The region is usually belt-shaped. The partial discoloured region is normally an independent region.

The partial discoloured region caused by unbalanced precipitation of Zr, as described above has been found to at least partly depend on the sulphur content. Consequently it is preferred to restrict the sulphur con-

tent, which may be an impurity in the alloy, to less than 0.005% by weight. If the sulphur content is less than 0.005% by weight, the number of partial discoloured regions caused by unbalanced precipitation of Zr can be 2 grains/100cm^2 or less. The said sulphur content is more preferably less than 0.004% by weight, but even more preferably less than 0.003% by weight. In addition, the number of partial discoloured regions caused by unbalanced precipitation of Zr has also been found to be at least partly influenced by the method of incorporating Zr in the alloy. Adding Zr in the form of a matrix alloy of Cu-Zr is preferable to reduce formation of said partial discoloured regions.

The preferred composition of the Cu alloy of the present invention can be specified by the following optional limitations.

If the Cr content is 0.1% by weight or more, the mechanical strength and heat resistance of the alloy are increased. This effect is maintained without impairing the bending strength and electrical conductivity of the alloy until the Cr content reaches 1% by weight. the value of the Cr content is preferably in the range from 0.2-0.6% by weight. The value of the Cr content is more preferably in the range from 0.2-0.5% by weight.

If the Zr content is 0.01% by weight or more, the mechanical strength and heat resistance of the alloy are increased. This effect is maintained without impairing the bending strength and electrical conductivity of the alloy until the Zr content reaches 0.5% by weight. The value of the Zr content is preferably in the range from 0.05-0.3%by weight. The value of the Zr content is more preferably in the range from 0.05-0.25% by weight.

The lead frame material of the present invention preferably has high electrical conductivity, which is not less than 75IACS%. If the conductivity is 75IACS% or more, a higly efficient lead frame can be made of the alloy for use with a highly integrated semiconductor element. The electrical conductivity of the lead frame is more preferably 80IACS% or more. The electrical conductivity of the lead frame is even more preferably 85IACS% or more.

In order to produce a lead frame with high electrical conductivity, the impurities in the alloy are preferably less than 0.05% by weight of Fe, less than 0.1% by weight of Ni, less than 0.05% by weight of P, less than 0.1% by weight of Sn and less than 0.1% by weight of Zn. The effects mentioned above can be maintained without impairing the electrical conductivity of the alloy, so long as any such impurity present does not exceed these preferred limits. The content of each of these elements is more preferably less than 0.05% by weight of Ni, less than 0.03% by weight of P, less than 0.05% by weight of Sn and less than 0.05% by weight of Zn.

The lead frame and the alloy material from which it can be made are improved if the following conditions are met.

First of all, the peeling part on the surface of the lead frame is preferably 5 grains/coil or less. If an IC package or a LSI package is produced using a lead frame with a peeling part on the surface of the lead frame of more than 5 grains/coil, a highly reliable package is not obtained, because of impairment of the yield production caused by the peeling parts.

Accordingly, the value of the peeling part is preferably not more than 3 grains/coil, and the value of the peeling part is more preferably zero. The term "peeling part" as used in this description and the claims means the condition when a portion of the surface peels linearly from the surface of the lead frame.

Additionally, a plating scab caused by heat treatment at the time of coating on the surface of the lead frame should not appear.

If an IC package or an LSI package is produced by the lead frame using the same lot which has a plating scab caused by the heat treatment, a highly reliable package is not obtained because of the high possibility of producing a plating scab at the time of use. The term "plating scab" as used in this description and the claims means a convex part which seems to be swollen up from the plating face.

Plating scabs can be detected by confirming the flattness of the plated face after performing plating, and thereafter by observing the surface by stereomicroscope (X 20) after performing hot working at 350°C for 5 minutes.

Third, the Vickers hardness of the lead frame is preferably 150Hv or more.

If the Vickers hardness is not less than 150Hv,a highly reliable package having sufficient hardness can be produced. The value of the Vickers hardness is preferably not less than 160Hv. The value of the Vickers hardness is more preferably not less than 170Hv.

Thus, by using copper alloys according to the prevent invention in the production of lead frames, high hardness and high electrical conductivity can be obtained. Morever, the yield of production and the reliability can be improved.

EXAMPLES

The present invention is now further described by way of non-limiting embodiments and some comparative examples.

Embodiments1-20

First, Cu alloy having the compositions as shown in Table-1 were prepared by casting after smelting under vacuum in a carbon crucible and an ingot was produced. Hot forging after heating to about 900°C was then performed in order to form each ingot to a billet having a thickness of about 150mm and a width of about 450mm. Next, hot rolling after heating to about 950°C was then performed in order to form each billet to a hot coil having a thickness of about 13mm and a width of about 450mm. After performing hot working at 750°Cto 800°C, in conclusion, a solution treatment was performed by rapid cooling.

After grinding the surface of the hot coil performed by the rapid cooling, as described above, cold rolling was then performed to roll each alloy to a plate having a thickness of about 2mm, and middle annealing was then performed to those coils at about 450°C for 6 hours. After that, surface polishing was performed, and then after performing cold rolling to roll each alloy to a plate having a thickness of 0.25mm, age-hardening at about 450°C for 6 hours was performed to obtain the lead frame.

As the surface condition of the lead frames having the compositions of sample Nos.1 to 20 obtained in this manner, the number of partial discoloured regions were investigated in the range of 10cmx10cm, and the average value of them was measured at 10 different ranges. Table-2 shows the results of the above mentioned evaluation. In addition, the Vickers hardness of the samples was measured, and the electrical conductivities were calculated by measuring relative resistance (at the normal temparature) using the four terminal method. Moreover, the number of peeling parts of about 2 tons of coils by weight were measured.

Each plate was punched to prepare a lead frame of a shape as shown in Fig.1. By using each of these lead frames, the presence of the plating scabs caused by heating treatment (a scab being a convex part which seems to be swollen up from the plating face) was decided by confirming the flattness of plated face after performing Ag plating, and thereafter by observing the surface by stereomicroscope (X 20) after performing hot working at 350°C for 5 minutes in an air atmosphere. The plating scab caused by heat treatment was examined in each of twenty frames for each sample, and the number of frames having the plating scabs is shown for each sample in Table-2. Table-2 also shows the plating scab evaluation results.

In addition, as comparison examples, lead frames made of conventional Cu alloys (which composition is shown in Table-1) were also evaluated similarly. Table-2 also shows the evaluation results.

As clearly shown in Table-2, when the content of sulphur in each material is less than 0.005% by weight, the partial discoloured regions on the surface of the lead frame are few. Thus, the peeling parts and the plating scabs caused by heat treatment and the like are fewer compared with the comparative examples B, Fig. 3 with many partial discoloured regions. This result contributes to improve the yield of production and reliability of the IC package and the like. In addition, it is found that keeping high conductivity is also achieved with a good reappearance, because of the content of impurities such as, Fe, Ni and the like is at a low level.

Moreover, from the view of Vickers hardness, lead frames with high hardness can be obtained which correspond to high efficiency.

The surface of the lead frame of the comparative example having many partial discoloured regions was observed by scanning electron microscope (JSM-T300, made by Japan Electron Optics Laboratory & Co., Ltd.; accelerated voltage 10KV, magnification 56.25 on the photograph).

Fig. 2 shows the results of the observation of a comparative example as a typical figure showing the surface of a lead frame by scanning electron microphotograph. As shown in Fig. 2, the partial discoloured region, part A, has whitish vertical lines in the centre. The partial discoloured region looks whitish by scanning electron microphotograph, since Zr on the surface is oxidized. Zr is easily oxidized in an air atmosphere because Zr is an active metal which reacts with oxygen. The Part A shaped line looks like a blackish line to the naked eye.

Figure 3 is a microphotograph (x 32) of a comparative example. The figure shows that the surface of this comparative lead frame has plating scabs B caused by the heat treatment.

Moreover, when the surface of the lead frame of the comparative example which has a partial discoloured region was analyzed by electron probe micronanalyser for which see the results in Figures 4a to 7b inclusive, (EPMA, made by Japan Electron Optics Laboratory & Co.,Ltd.), Zr, S and O were detected from the partial discoloured region.

The results of the comparative surface analysis of the same region of the lead frame shown in Figures 4a to 7b inclusive, demonstrate that unbalanced precipitation of Zr appeared at the part having enough S content, and the partial discoloured region was caused by this unbalanced precipitation of Zr. On the other hand, outside the partial discoloured region, neither Zr or S were detected. O was detected since Zr was oxidized after being exposed to an air atmosphere. Fig. 4b shows Zr detection, Fig. 5a shows S detection and Fig. 6b shows the oxygen detection.

As described above, according to the lead frame of the present invention, excellent surface conditions are obtained, making it possible to prevent the deterioration of the yield of production of IC, LSI and the like caused

by defects on the surface of the lead frame. In addition, the lead frame according to the present invention remarkably contributes to the improvement of the reliability.

Table 1

		Alloy Component (wt%)								
		Cr	Zr	S	Fe	Ni	P	Sn	Zn	Cu
Example	1	0.76	0.41	0.001	0.014	0.055	0.011	0.018	0.019	balance
	2	0.54	0.28	0.002	0.029	0.061	0.023	0.014	0.009	〃
	3	0.32	0.14	0.001	0.005	0.046	0.031	0.021	0.005	〃
	4	0.22	0.09	0.001	0.004	0.024	0.004	0.006	0.002	〃
	5	0.36	0.20	0.0007	0.015	0.020	0.014	0.011	0.022	〃
	6	0.41	0.15	0.0004	0.006	0.055	0.001	0.001	0.006	〃
	7	0.30	0.16	0.0001	0.009	0.018	0.018	0.009	0.018	〃
	8	0.33	0.13	0.0001	0.023	0.033	0.011	0.014	0.009	〃
	9	0.46	0.10	0.003	0.039	0.043	0.001	0.024	0.007	〃
	10	0.51	0.33	0.0001	0.014	0.018	0.007	0.009	0.006	〃
	11	0.32	0.11	0.0001	0.027	0.041	0.031	0.071	0.021	〃
	12	0.23	0.05	0.004	0.005	0.022	0.001	0.007	0.009	〃
	13	0.41	0.12	0.0003	0.010	0.015	0.005	0.021	0.002	〃
	14	0.31	0.10	0.0004	0.014	0.032	0.022	0.011	0.067	〃
	15	0.28	0.03	0.001	0.013	0.024	0.002	0.029	0.023	〃
	16	0.61	0.32	0.0007	0.006	0.052	0.004	0.030	0.005	〃
	17	0.92	0.07	0.0009	0.013	0.016	0.001	0.005	0.007	〃
	18	0.28	0.26	0.0008	0.016	0.014	0.023	0.018	0.035	〃
	19	0.45	0.15	0.003	0.032	0.056	0.022	0.021	0.019	〃
	20	0.24	0.08	0.001	0.004	0.045	0.012	0.014	0.006	〃
Comparative Example	1	0.34	0.18	0.006	0.026	0.020	0.012	0.210	0.084	〃
	2	0.28	0.10	0.008	0.098	0.033	0.031	0.068	0.162	〃
	3	0.46	0.23	0.007	0.044	0.013	0.073	0.117	0.024	〃
	4	0.61	0.32	0.008	0.021	0.136	0.022	0.067	0.023	〃
	5	0.22	0.08	0.009	0.081	0.056	0.019	0.029	0.006	〃

Table 2

		Partial discolored region (grains/100cm²)	Vickers Hardness (Hv)	Conductivity (IACS %)	Peeling part (grains/coil)	The number of frames having plating scab (/20 frames)
Example	1	0	181	81.2	3	0
	2	1	168	82.5	0	0
	3	0	171	84.3	1	0
	4	0	172	89.4	0	0
	5	0	158	83.1	1	0
	6	0	164	90.2	0	0
	7	0	175	82.0	0	0
	8	0	176	84.0	0	0
	9	0	165	88.6	0	0
	10	0	172	82.4	0	0
	11	0	178	82.0	0	0
	12	1	158	91.1	1	0
	13	0	169	85.0	0	0
	14	0	180	83.0	0	0
	15	0	154	90.8	0	0
	16	0	174	79.2	0	0
	17	0	163	83.6	1	0
	18	0	171	82.8	0	0
	19	2	165	84.1	1	0
	20	0	168	88.2	0	0
Comparative Example	1	7	167	69.3	11	4
	2	9	162	71.4	15	3
	3	7	170	68.6	12	5
	4	10	182	67.5	10	4
	5	8	165	72.3	8	5

Claims

1. A copper alloy containing 0.1 to 1 % by weight of chromium, 0.01 to 0.5% by weight of zirconium and having partial discoloured regions caused by unbalanced precipitation of the zirconium distributed thereon at a rate of 2 grains/100cm^2 or less, the balance being substantially copper.

2. An alloy according to claim 1, which contains less than 0.005% by weight of sulphur.

3. An alloy according to claim 1 or 2, which contains less than 0.05% by weight of iron, less than 0.1% by weight of nickel, less than 0.05% by weight of phosphorus, less than 0.1% by weight of tin and less than 0.1% by weight of zinc.

4. An alloy according to any preceding claim, whose conductivity is not less than 75IACS%.

5. A lead frame constructed of or otherwise comprising a copper alloy as claimed in any preceding claim.

6. A lead frame according to claim 5, wherein a peeling part on the surface of the lead frame does not exceed more than 5 grains/coil.

7. A lead frame according to claim 5 or 6, wherein there is one or less plating scab caused by heat treatment.

8. A lead frame according to any one of claims 5 to 7, wherein the Vickers hardness of said lead frame is not less than 150 Hv.

9. An integrated circuit or LSI component which incorporates a lead frame as claimed in any one of claims 5 to 8.

10. Use of a copper alloy as claimed in any one of claims 1 to 4 in the fabrication of lead frames.

FIG. 1

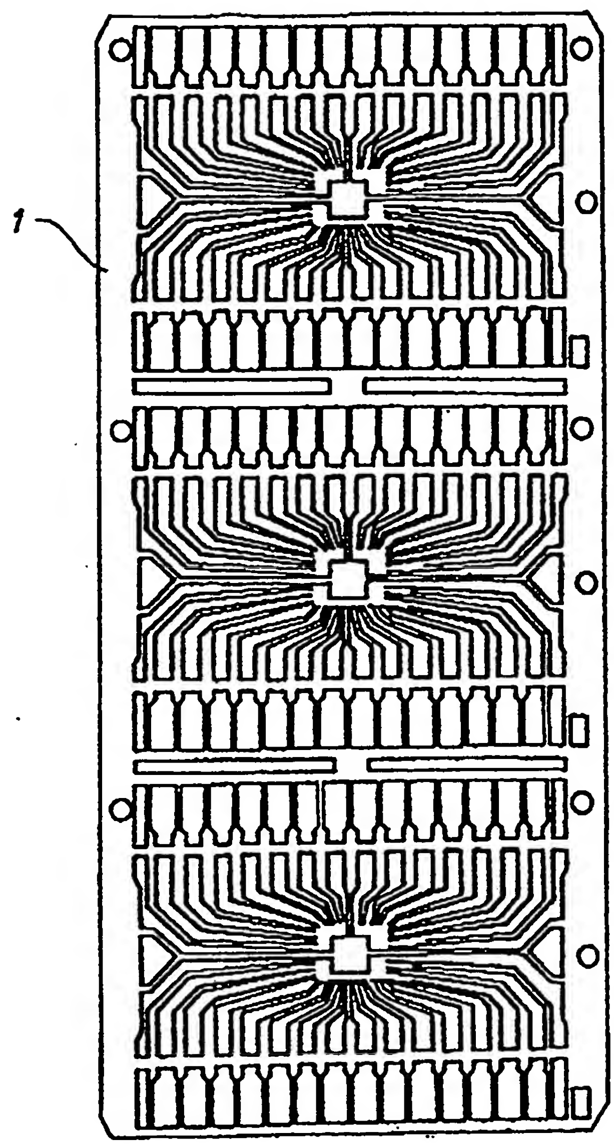


FIG. 2

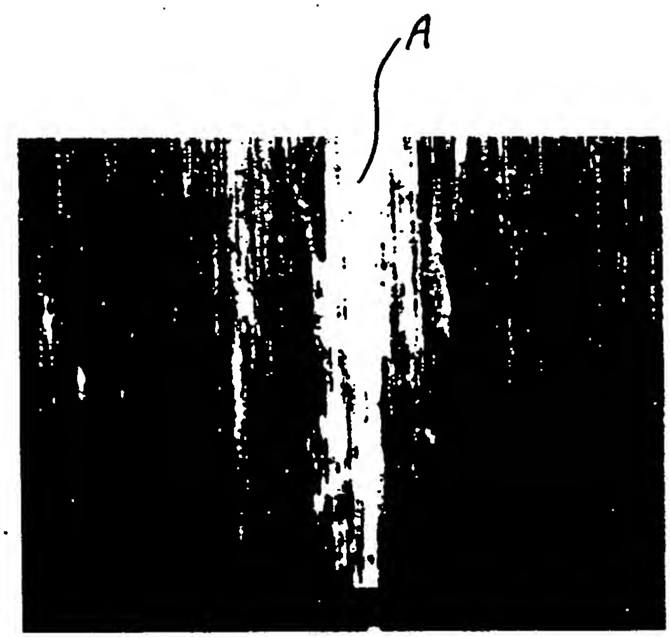


FIG. 3

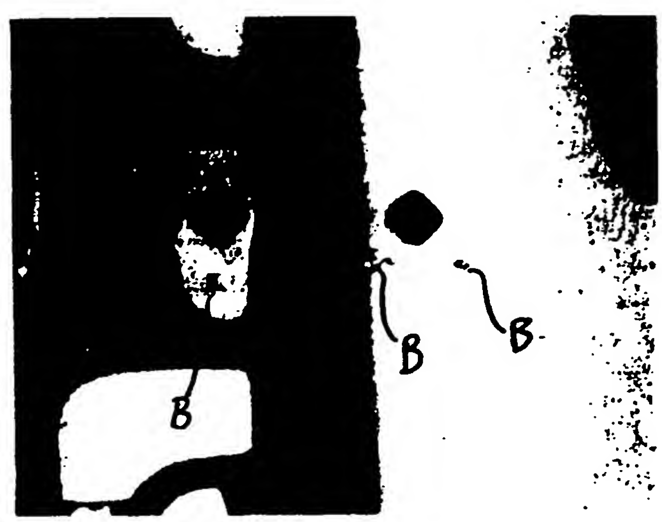


FIG 4a

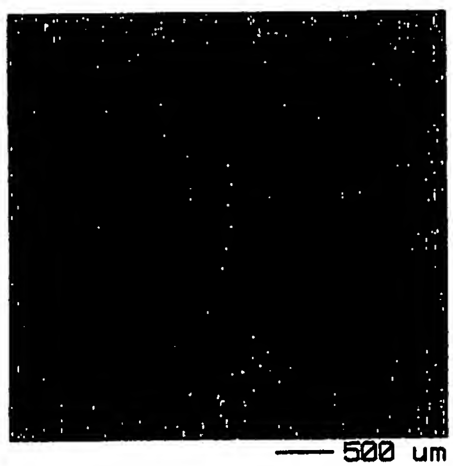
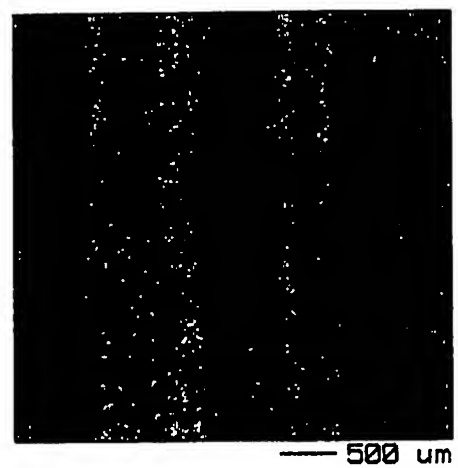

500 um

FIG 4b


500 um

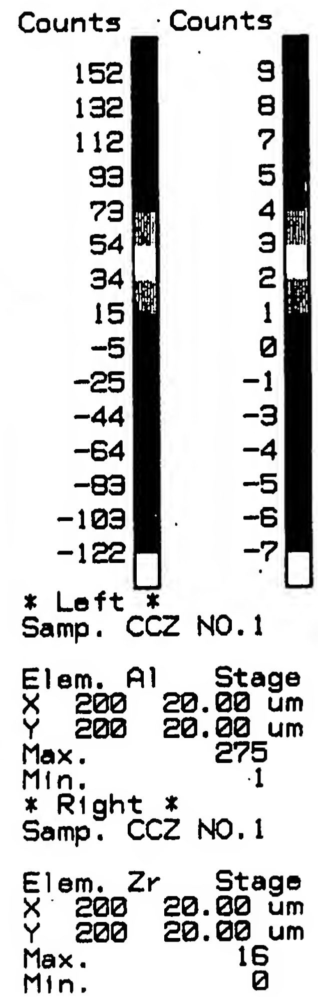
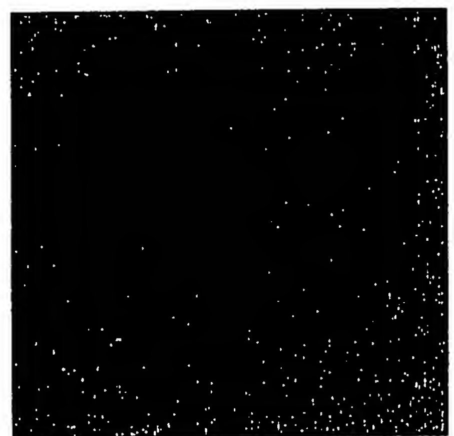
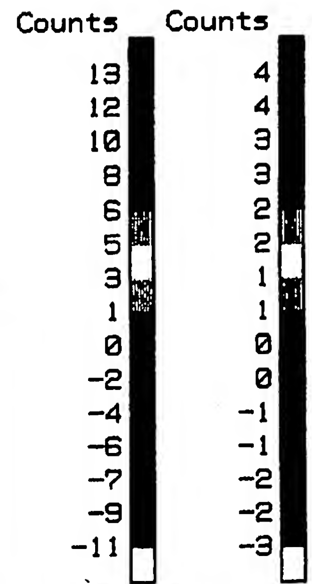

Counts
152
132
112
93
73
54
34
15
-5
-25
-44
-64
-83
-103
-122
Counts
9
8
7
5
4
3
2
1
0
-1
-3
-4
-5
-6
-7
* Left *
Samp. CCZ NO.1
Elem. Al Stage
X 200 20.00 um
Y 200 20.00 um
Max. 275
Min. 1
* Right *
Samp. CCZ NO.1
Elem. Zr Stage
X 200 20.00 um
Y 200 20.00 um
Max. 16
Min. 0

FIG 5a

FIG 5b





* Left *
Samp. CCZ NO.1

Elem. S Stage
X 200 20.00 um
Y 200 20.00 um
Max. 24
Min. 0
* Right *
Samp. CCZ NO.1

Elem. C Stage
X 200 20.00 um
Y 200 20.00 um
Max. 7
Min. 0


Counts
7
6
5
5
4
3
2
2
1
0
0
-1
-2
-3
-3
Counts
71
62
54
46
38
30
22
14
5
-3
-11
-19
-27
-35
-43
* Left *
Samp. CCZ NO.1
Elem. P Stage
X 200 20.00 um
Y 200 20.00 um
Max. 10
Min. 0
* Right *
Samp. CCZ NO.1
Elem. O Stage
X 200 20.00 um
Y 200 20.00 um
Max. 114
Min. 0

FIG 6b

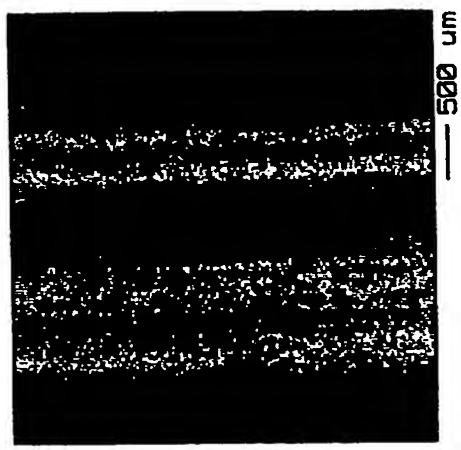

500 um

FIG 6a

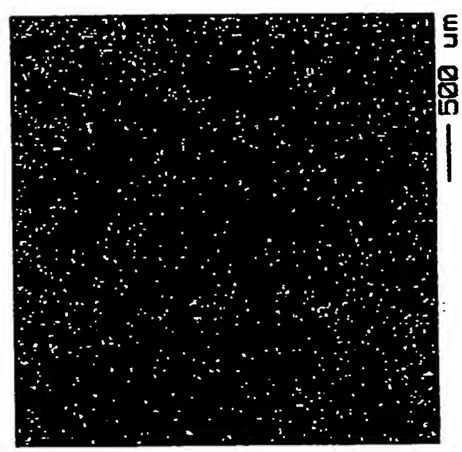

500 um

FIG 7a

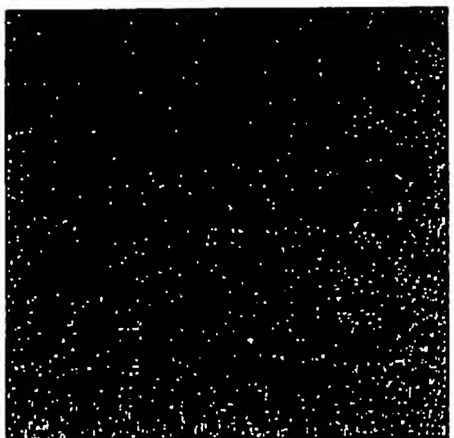
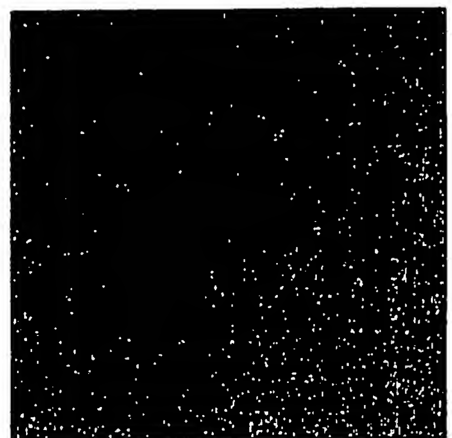
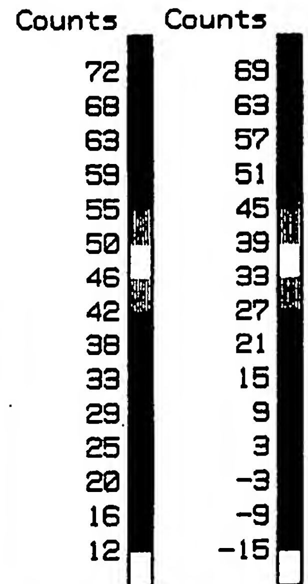


FIG 7b





* Left *
Samp. CCZ NO.1

Elem. Si Stage
X 200 20.00 um
Y 200 20.00 um
Max. 77
Min. 17
* Right *
Samp. CCZ NO.1

Elem. Cr Stage
X 200 20.00 um
Y 200 20.00 um
Max. 91
Min. 7

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 31 1805

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 114 338 (TOKYO SHIBAURA DENKI K.K.) * claims 1-5 *	1,3,5	C22C9/00 H01L23/495
X	*page 6, Table*	8	
Y	GB-A-2 219 473 (MITSUBISHI KINZOKU K.K.) * claims 1-4 *	1,3,5	
Y	GB-A-2 181 742 (MITSUBISHI KINZOKU K.K.) * claims 1-8 *	1,3,5	
A	DE-C-3 527 341 (WIELAND-WERKE AG) * the whole document *	1-10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C22C
H01L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13 FEBRUARY 1992	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)